ADVANCED DEVICES LABORATORY

Research Center for the Airtron Division of Litton Industries 200 East Hanover Avenue, Morris Plains, New Jersey

296 183

THIRD INTERIM DEVELOPMENT REPORT

FOR

DEVELOPMENT OF A FERRITE MATERIAL

FOR A HIGH POWER PHASE SHIFTER

AT S-BAND

This report covers the period 18 October 1962 to 18 January 1963

AIRTRON, A DIVISION OF LITTON INDUSTRIES

200 EAST HANOVER AVENUE

MORRIS PLAINS, NEW JERSEY

NAVY DEPARTMENT BUREAU OF SHIPS ELECTRONICS DIVISION

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2. PURPOSE

The purpose of this contract is to develop a ferrite material suitable for operation at 250 Kw peak power in a phase shifter device operating at S-band frequencies. This work will primarily be centered around the nickel aluminum gallium ferrite system. Better insight into the behavior of this system will be obtained by measuring the microwave properties as a function of power level. It is anticipated that a Reggia-Spencer type phase shifter will be constructed utilizing a ferrite in this new system.

3. <u>MATERIAL DEVELOPMENT</u>

3.1 Compositional Study

At the initiation of this program, the basic requirements that the material to be developed should meet were, saturation magnetization approximately 600 gauss, Curie temperature 200°C and the loss tangent less than 0.005 at S-band. As a result of the compositional studies made, two compositions NAGS-3 and NAGS-4 essentially met these specifications. As will be discussed in a later section, NAGS-4 was selected as the composition as having the best chance of fulfilling all the requirements demanded for operation at S-band in a phase shift device at 250 Kw. Unless high power and phase shift data dictate otherwise, this portion of the program will be considered complete.

3.2 Ceramic Processing

So that we may better understand the effect of ceramic processing on the properties of ferrites in the nickel aluminum gallium iron system, a number of experiments have been started. The composition for all these experiments is NAGS-4. In order to minimize the number of variations, all batches are of the same total weight. The ratio of batch size to weight of balls and water have been kept constant for all ball millings. A total of 12 batches have been prepared. They were milled for 6, 12, 24, and 48 hours. Three batches at each milling time were prepared. One batch from each milling time were calcined at 1050°C, 1125°C, and 1200°C. During the coming quarter, these materials will be pressed at various pressures and

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MATERIAL DEVELOPMENT (Continued)

fired at several temperatures and evaluated to ascertain the effect of ceramic processing on the properties of this material.

3.3 Flame Spraying

The flame spray apparatus has been constructed and four batches have been flame sprayed. A diagram of the apparatus is shown in Figure 1.

The sidearm and tank were fabricated entirely from 304 stainless steel as are both the flame spray and scrubber nozzles. The shaded areas shown in Figure 1 indicate the areas where the powder collects.

NAGS-5-2, ($Ni_{1.00}Ga_{0.267}Al_{0.733}Fe_{1.00}O_4$), was the first flame spray material prepared using the apparatus described above. A 2000 gram batch of nitrate salts in the mole ratio indicated was dissolved in methanol with the exception of the gallium. The gallium was not added as the nitrate due to the difficulty in obtaining gallium nitrate with a known amount of attached water at a reasonable price. Since gallium oxide is available in high purity, the amount of gallium as the oxide was weighed out and put into solution with nitric acid. This was then evaporated to dryness and added to the methanol solution of nickel, aluminum and ferric nitrate. While putting these materials into solution, it was noted that the gallium was the last material to go into solution and required an extended period of mixing. This was attributed to the fact that the gallium was evaporated to too dry a condition, probably driving off some of the attached water. The specific gravity of the completed solution was 1.245.

Figure 1

Flame Sprayer
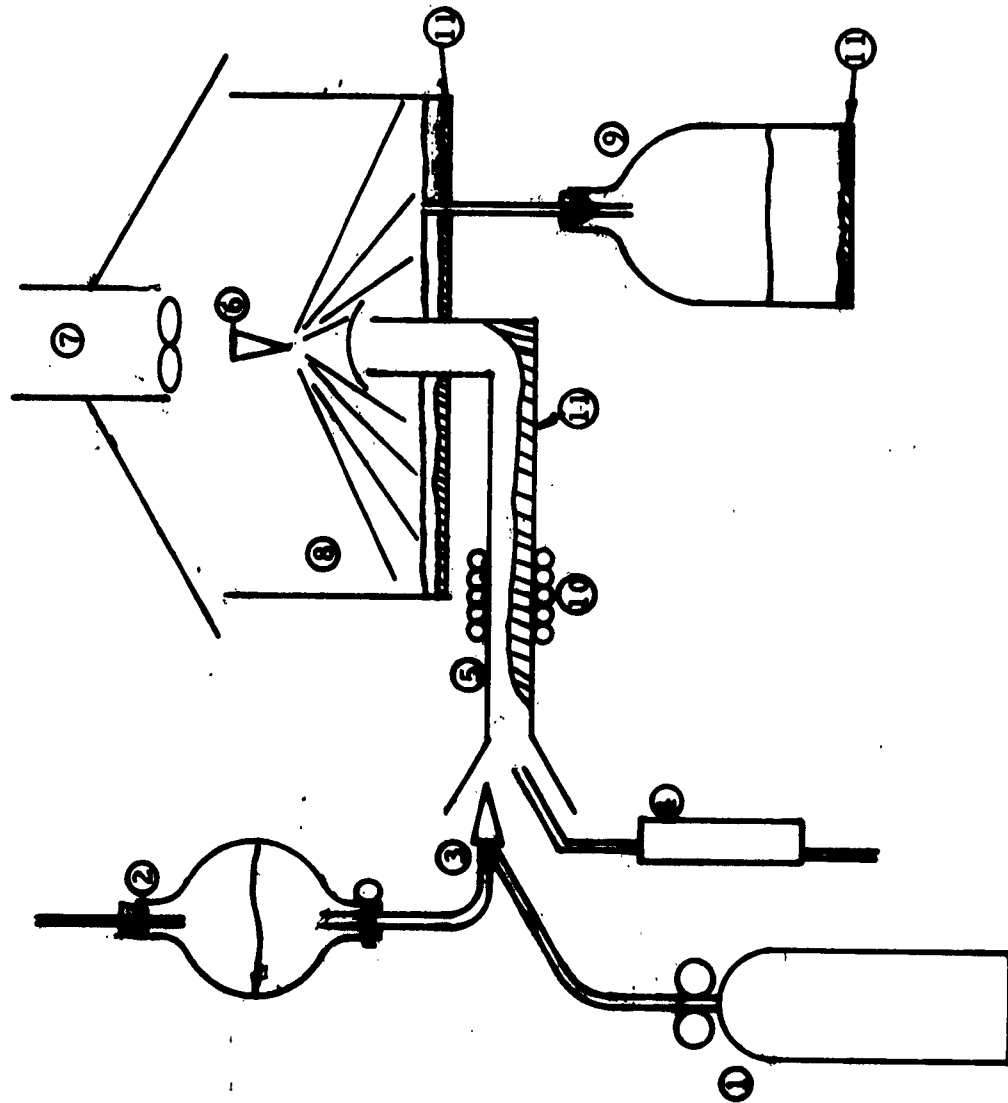
1. Oxygen feed
2. Solution feed (gravity or pressure)
3. Two fluid spray nozzles
4. Auxiliary air acetylene torch
5. Sidearm
6. Gas scrubber (water)
7. Exhaust fan and hood
8. Tank
9. Bottle containing fines
10. Cooling coil
11. Ferrite Powder

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MATERIAL DEVELOPMENT (Continued)

A low volume, high velocity oxy-acetylene torch was used at the start of the first run. It was found that this type torch was not suitable for three reasons.

1. There was ineffective burning of the solution which was evidenced by the light-brown color of the collected powder.

2. An oxidizing flame was very difficult to obtain.

3. Carbon deposited at the nozzle tip and put out the flame.

For these reasons, a high volume air-acetylene torch was substituted during the run. Based on a 100 percent conversion of the nitrate solution to spinel, the theoretical yield would be 680 grams. The actual yield of NAGS-5-2 was close to 150 grams, 70 percent of which was collected in the sidearm, the remainder being evenly divided between the bottles and tank. This was only a 22 percent yield which was less than anticipated. The poor yield is attributed to three major factors.

1. The scrubber nozzle was not effective. Approximately 50 gallons of water were needed to collect 50 grams of material or about 1 gram per gallon of water was collected. It appears as though very fine misting nozzles used in a high column would increase the yield of fines. Also, if the velocity of the gas and powder could be decreased, more material would be collected.

2. The specific gravity of the liquid was low which would reduce the particle size of this material hurled down the sidearm and

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MATERIAL DEVELOPMENT (Continued)

much of the material would be carried up the stack with the resultant gases.

3.   Poor burning conditions allowed material to pass out the flue or go back into solution in the water during the scrubbing operation.

The material collected was kept separate and is distinguished by the following symbols:

SA   -   Entire sidearm yield

Fr   -   Front 1/3 sidearm yield

Mi   -   Middle 1/3 sidearm yield

Ba   -   Back 1/3 sidearm yield

Ta   -   Material settled in tank

Fi   -   Material settled in bottles

Subsequent flame spray runs will also be distinguished by the above symbols.

NAGS-5-2 was processed in the following manner preparatory to firing:

1.   All the powder was burned at 950°C in air for 2 hours to rid the material of any water vapor, unreacted nitrates, and unoxidized carbon. This burning operation appeared to darken the color of the material slightly. Also, of note, was the different shade of brown between the sidearm material and the tank and bottle material.   The tank and bottle material was lighter in color indicating a finer particle size.

2.   Six percent Cerimal "C" binder was added to a slurry of water and powder.

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MATERIAL DEVELOPMENT (Continued)

3. The water was evaporated and the dried material was screened through 60 mesh and pressed at 250,000 psig to increase densification of the powder.

4. The material was again screened through 60 mesh and pressed into bars suitable for firing and hot pressing.

5. The binder was burned off.

NAGS-6-1, $(Ni_{1.00}Ga_{0.267}Al_{0.733}Fe_{0.980}O_4)$, was prepared in a similar manner as described above. The only change in procedure was that the gallium was not evaporated to dryness but added as the nitrate solution of the oxide with no evaporation.

Composition 6-1 was flame sprayed using a high volume air-acetylene torch. The specific gravity of the solution was 1.325. Approximately 225 grams of powder was collected. This was a yield of slightly over 29 percent, or a 7 percent increase over NAGS-5-2. The higher yield was due to better burning conditions plus an increase in density of the solution. The major loss of material was up the stack indicating that the scrubber is not capable of removing the very fine particles from the exhaust gases.

NAGS-5-3, $(Ni_{1.00}Ga_{0.267}Al_{0.733}Fe_{1.00}O_4)$, was prepared as above and flame sprayed except that two high volume air-acetylene torches were used instead of one. The torches were placed on either side of the

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MATERIAL DEVELOPMENT (Continued)

spray nozzle and impinged on the spray.

The material collected in the sidearm was a very deep brown-gray color indicating a higher burning temperature. The material collected in the tank and bottle was light-brown indicating a finer particle size.

The yield for NAGS-5-3 was approximately 30 percent. The powder was further processed as previously described except that the calcining or burn off temperature was raised 100°C to 1050°C.

Further design changes were made to increase the efficiency of the burning of the spray. A ring was designed and build which would completely encircle the spray nozzle and the ring was shaped so that the acetylene flame would focus at a point 2 inches from the nozzle tip.

The hollow ring consisted of 32 holes drilled at the proper angle to achieve this. The following faults were observed in this design:

1. The holes were of too large a diameter for the flow causing burning of the acetylene in the hollow ring.

2. The acetylene did not enter tangentially into the ring caus- ing uneven flame length. The longer flames were emitted from the holes directly in the path of the incoming acetylene.

The apparatus has been redesigned and is in the process of being built.

NAGS-4-3, $(NiO)_{0.98}(MnO_2)_{0.02}(Ga_2O_3)_{0.124}(Al_2O_3)_{0.364}(Fe_2O_3)_{0.462}$,

MATERIAL DEVELOPMENT (Continued)

was flame sprayed as described above. The specific gravity of the solution
was 1.275. Because of the decrease in specific gravity, the yield was reduced
to approximately 25 percent. This is about the same yield obtained for
NAGS-5-2 which had about the same specific gravity. This composition was
prepared to compare the flame sprayed material with conventionally prepared
material.

3.4 Hot Pressing

A large hot pressing die, designed to produce ferrite samples
1 inch x 1 inch x 6 inches is presently being fabricated. The outer stainless
steel box has been completed. The zirconia and alumina slabs have been pur-
chased. Various hydraulic parts for the 400 ton press have been purchased.
The press modifications are necessary so that the rate of closure of the press
can be accurately controlled and the pressure required accurately maintained.
The die and press are scheduled to be completed in February 1963.

A hot pressing run HP-23 was made using NAGS-4-2 material
$(NiO)_{0.98}(MnO_2)_{.02}(Al_2O_3)_{0.364}(Ga_2O_3)_{0.124}(Fe_2O_3)_{.4125}$.
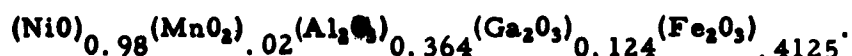
The green prepressed bar was first annealed in oxygen at 1050°C
for 72 hours in an attempt to oxidize any iron picked up during milling. The
bar was then hot pressed in the following manner. The pressure in the die was
4000 psi, the temperature was raised to 1150°C and held for 45 minutes.

Another run, HP-24, was made using the fines collected in the tank

<u>MATERIAL DEVELOPMENT</u> (Continued)

from the flame spraying of NAGS-6-1-Ta, $(NiO)_{1.00}(Ga_2O_3)_{.133}(Al_2O_3)_{.367}(Fe_2O_3)_{0.49}$.

This was the first attempt to hot press a flame sprayed powder and was carried out under the following hot pressing conditions. The pressure was 4000 psi, temperature was raised to 1150°C and held for 30 minutes.

The sample was dense and extremely brittle and was cracked in numerous places but remained in one piece. When the bar was purposely cracked, the fracture appeared to be concoidal, indicating a very vitreous sample. These cracks were quite possibly due to thermal shock.

Another attempt was made to hot press flame sprayed material using NAGS-5-2-Ta, $(NiO)_{1.00}(Al_2O_3)_{.367}(Ga_2O_3)_{.133}(Fe_2O_3)_{.50}$. This was run HP-25.

This bar was hot pressed at 4000 psi at 1100°C for 30 minutes. This bar did not crack and had much greater porosity than HP-24.

4. **MEASUREMENT APPARATUS**

4.1 <u>Tan δ at S-band</u>

In the last report, it was mentioned that cavity Q should decrease when a sample is inserted in the cavity. For some low loss samples, it was found that the cavity Q increased. It has been found that this anomaly was due to the large size of the coupling holes in the cavity. The loaded cavity is given by:

$$\frac{1}{Q_L} = \frac{1}{Q_e} + \frac{1}{Q_c}$$

Q_e is the external Q which is dependent on the coupling hole size and Q_c is the unloaded Q which is dependent on the losses of the cavity walls and the dielectric loss of the cavity interior. If Q_e is sufficiently large, then any change in Q_L is caused by a change in the dielectric loss of the cavity interior. The coupling holes of the TM_{012} cavity have now been made small enough so that the required condition on Q_e is actually obtained.

The tan δ setup now yields results which are felt to be consistent with published results which have been obtained for Al_2O_3 (WesGo-AL-300) and TT-414.

Airtron Measurements at 3200 Mc/s	ϵ'	Tan δ
WesGo-AL-300 Al_2O_3 .208 dia.	9.78	.00034
WesGo-AL-300 Al_2O_3 .103 dia.	9.38	.00031
TT-414 .208 diameter	12.8	.00042

MEASUREMENT APPARATUS (Continued)

Reported Values	ϵ'	Tan δ
Trans. Tech. TT-414 (Measuring frequency not given)	11.5	.0005
WesGo-AL-300 Al_2O_3 (Measured at 1000 Mc/s)	9.00	.00030

The differences between the published data and the dielectric constant ϵ' measured at Airtron is felt to be due to sample size. It is seen that as the size of the Al_2O_3 is decreased, the value of ϵ' approached the published value.

However, in order to keep the ϵ'' measurements as reliable as possible, it is desirable to use the largest possible sample.

We have attempted to measure the tan δ at S-band of several standard production ferrites of different compositions. The following problem was encountered which may explain the high loss in several of the NAGS samples measured.

The ferrites measured were nickel aluminum ferrites with saturation of 1400 gauss and magnesium manganese ferrite with a saturation of 2000 gauss. Both these materials have been manufactured for many years and are known to have low dielectric loss tangents. These materials, when checked in the S-band setup, and had a tan δ in the range of .0X. This is very unlikely. The diameter of the rod was then made smaller and the loss was reduced but not below .01. The fact that the loss did come down but is still high indicates that the rod is not in a part of the cavity where the H field is zero. The high saturation magnetization would give an apparent high tan δ in the presence of an H field.

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MEASUREMENT APPARATUS (Continued)

For materials that do have a sufficiently low saturation for measurement at S-band but have a high zero field loss, this would show up as a high apparent tan δ with presence of a small H field.

Figure 2a is a cross section at the center and perpendicular to the end plates of the TM_{012} cavity. The ferrite sample is suspended at the center with polystyrene holders (not shown).

Figure 2b shows the shape amplitude of the radial RF magnetic field at a plane through the center of the cavity parallel to the end plates. The amplitude is constant as one travels about the B-B' axis at a fixed radius from the center. This holds true for any plane parallel to the end plates. However, as one travels up and down the ferrite rod from the plane A-A', the maximum value Hm decreases to zero at the rod ends.

As the diameter of the ferrite rod increases from zero (completely unperturbed cavity), it begins to intercept some RF magnetic. If the zero field $(H_{d.c.} = 0)$ loss is very low then the magnetic loss introduced by the ferrite sample will be negligible and the assumption that all the loss introduced by the sample is dielectric loss will be correct.

This explains why the loss tangent obtained for TT-414 is the usually low value. However, as the saturation magnetization of the ferrite increases, the zero field loss at S-band increases. This explains why the higher saturation magnetization ferrites show abnormally higher loss tangents when measured at S-band.

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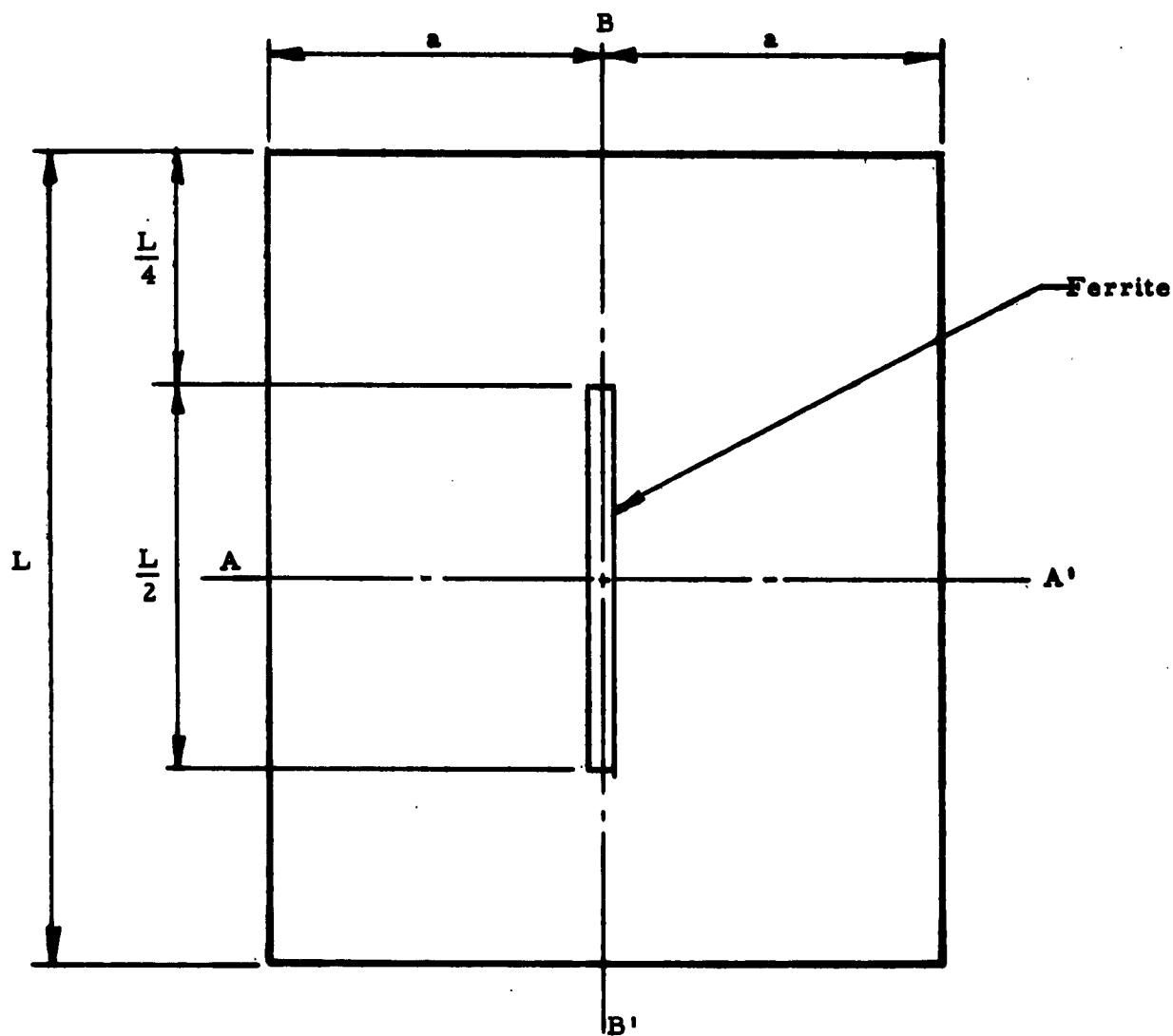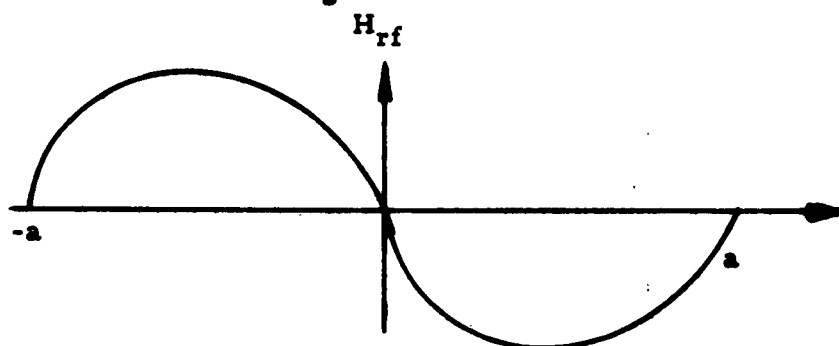
Figure 2a

Figure 2b

Cross Section of TM_{012} Cavity and the Radial RF Magnetic Field

MEASUREMENT APPARATUS (Continued)

In the future, it may be necessary to use smaller diameter samples even for NAGS ferrites with low saturation. This will eliminate any possibility of the zero field loss effecting the value of tan δ .

The S-band tan δ apparatus has been modified from previous setups in order to increase its sensitivity. This has been accomplished by adding a traveling wave tube amplifier before the bridge. Figure 3 is a schematic of the revised tan δ apparatus.

4.2 Line Shape and χ', χ''

The TE_{111} cavity for the line shape measurement has been constructed. Sample holders have been made for .150 and .100 diameter spheres. Spheres of these diameters of the various NAGS materials have been ground. We are presently awaiting the return of the LFE Stalo to evaluate the constructed apparatus. We have had two breakdowns with this piece of equipment; although minor, they have caused considerable delay.

4.3 High Power Loss vs. Peak Power

This measurement is awaiting the completion of the tube adapter required to use the high power tube which operates at 3400 Mc.

4.4 Phase Shift Measurement

We are attempting to measure the phase shift using relatively small samples. This is so we can obtain some relative figure of merit between samples without having to make large bars 1 inch x 1 inch x 6 inches. A device has been made which uses the actual samples ground for the tan δ measurement.

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Figure 3

Block Diagram for Measuring χ and Loss Tangent at S-Band

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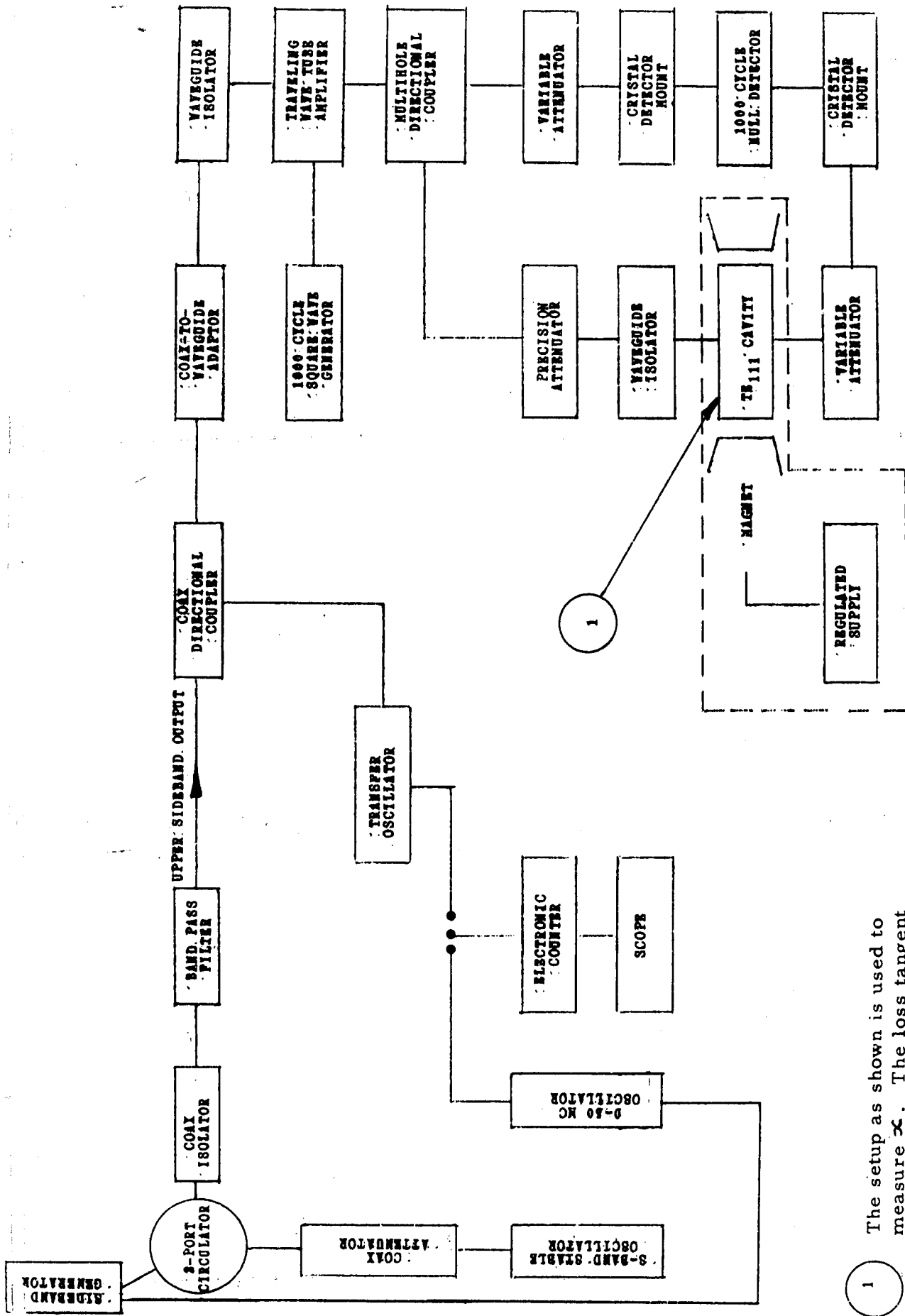
The setup as shown is used to measure χ. The loss tangent measurement is made by the substitution of a TM_{012} cavity and the elimination of the magnet.

MEASUREMENT APPARATUS (Continued)

The ferrite with dielectric tapers is placed along the transverse axis of a doubly ridged guide as shown in Figure 4. This is the ridge guide analogue of the Reggia-Spencer phase shifter.

A TT-414 sample was tried and very little phase shift was observed. Because of the small sample size, little phase shift is expected. In order to measure the small amount of phase shift, a new setup will be constructed. This will be accomplished by the use of a slotted line detector probe and a spring loaded dial micrometer capable of measuring movements of .0001 of an inch which is attached to the ridge guide slotted line.

Since the phase shifter we are testing is reciprocal; that is, phase shift measured in either direction through it is the same, it is not necessary to use a bridge to measure phase shift. Figure 5 is a block diagram of the setup used. When a matched low loss reciprocal phase shifter is inserted between a slotted line and a high quality short, the shift in the standing wave minimum is exactly equal to the phase shift produced by the phase shifter. Thus, by measuring the shift of the slotted line probe, the phase shift of the device can be measured.

The setup shown in Figure 5 can also be used to measure loss when the short is removed and replaced by a detector.

Data should be forthcoming for all the NAGS samples in the next report using this more accurate setup.

Cross Section of
Ridged Waveguide

Ferrite located here along this axis

H_o

Aluminum Oxide

Ferrite

Aluminum Oxide

3.0"

2.32"

3.0"
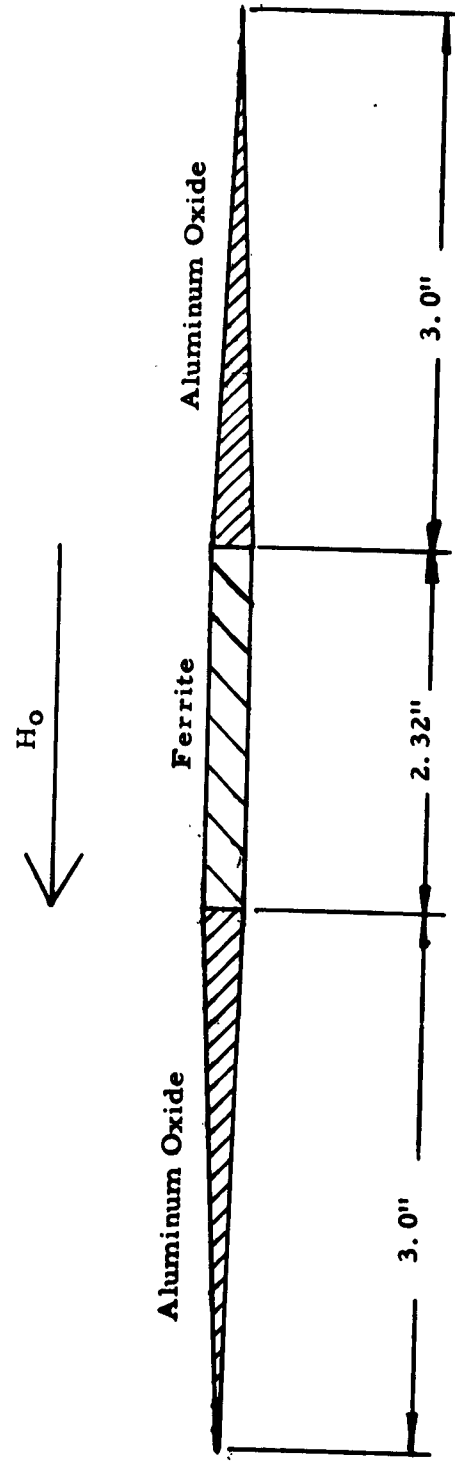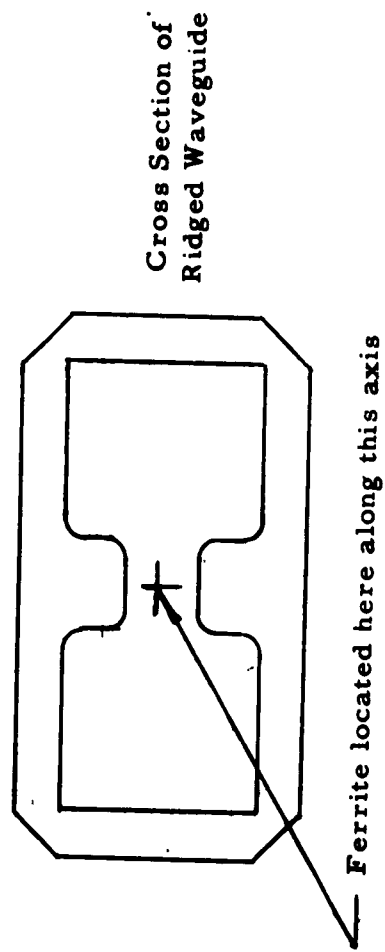
Figure 4

Phase Shift Device and Ferrite Sample

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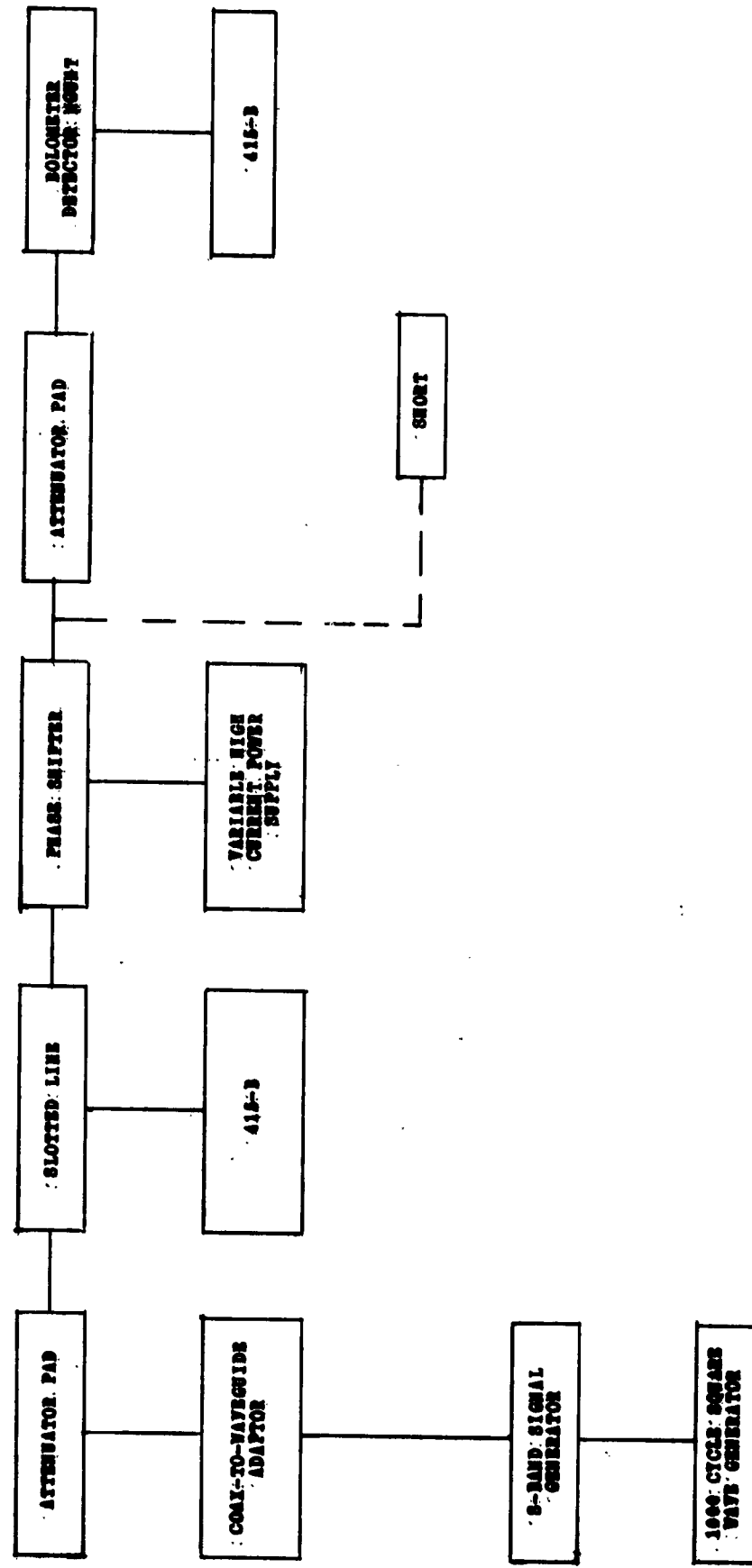
Figure 5

Block Diagram for Measuring Phase Shift and Loss vs. Field

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5. DISCUSSION OF THE DATA

5.1 Compositional Study

A series of compositions were prepared at the start of this program which was anticipated would meet the conditions required for a phase shift device at S-band. These conditions are: $4\pi M_s \sim 600$ gauss, $\tan \delta < 0.005$, and a Curie temperature of 200°C. In the nickel aluminum gallium system, it is possible to obtain a series of compositions that meet the Curie temperature and saturation requirements by the proper selection of x and y in the general formula $NiAl_xGa_yFe_{2-(x+y)}O_4$.

The compositions listed below were prepared anticipating that they would approach the required properties given above.

Composition	Tot. Sub. (x+y)	Al/Ga Ratio x/y	
NAGS-1 $Ni_{.98}Mn_{.02}Al_{.767}Ga_{.383}Fe_{.800}O_4$	1.15	2.0	Iron deficient
NAGS-2 $Ni_{.98}Mn_{.02}Al_{.750}Ga_{.300}Fe_{.900}O_4$	1.05	2.5	Iron deficient
NAGS-3 $Ni_{.98}Mn_{.02}Al_{.733}Ga_{.267}Fe_{.95}O_4$	1.00	2.75	Iron deficient
NAGS-4 $Ni_{.98}Mn_{.02}Al_{.728}Ga_{.248}Fe_{.934}O_4$	.975	2.95	Iron deficient
NAGS-5 $Ni_{1.0}Al_{.733}Ga_{.267}Fe_{1.0}O_4$	1.00	2.75	Stoichiometric

The evaluation of the properties of NAGS-1 through NAGS-5 prepared by conventional techniques have been completed. The properties for each composition

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DISCUSSION OF THE DATA (Continued)

are listed in Table I and are an average of several firings and of several samples from each firing.

From Table I it can be seen that the selection of the values of (x+y) for NAGS-1 and NAGS-2 were too large and a Curie temperature much less than 200°C were obtained.

One of the most interesting and important results that can be observed from these data is the fact that when the samples have been fired sufficiently high so that the porosity is less than 5 percent, the saturation magnetization increases drastically and both the 20 Mc and the S-band loss tangents increase. As will be shown later, the annealing experiments were inconclusive and could not explain these changes in properties with firing conditions.

Experience with other ferrites in the nickel aluminum iron systems have shown similar perplexing results. It has been observed in these other materials that when they are fired to high densities, i.e., low porosity, the saturation magnetization changes drastically (50 to 100 percent) and the microwave loss tangent increases. In the case of materials with compositions beyond the compensation point, the saturation magnetization reduced when fired to high densities. A possible explanation for these effects is given below.

The theory can be briefly stated as follows: when a ferrite is fired to a sufficiently high temperature to reduce the porosity to a very low value, the input thermal energy is no longer required to produce sintering and the reduction of pores but produces grain growth. As the grains grow, it may be possible for

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TABLE I

	$4\pi M_s$	T_c	Porosity	A.S.G.	20 Mc Tan δ	S-band Tan δ	ΔH X-band	"g"
NAGS-1	565	124	>5 %	5.0	.003	.001	200	2.8
NAGS-2	560	165	>5 %	5.0	.004	.003	250	3.0
NAGS-2	720	165	<1 %	4.95	.01	.005	225	2.8
NAGS-3	550	185	>5 %	5.0	.003	.003	225	3.2
NAGS-3	770	190	<1 %	4.97	.003	.010	275	2.7
NAGS-4	605	198	3 %	4.95	.002	.009	320	2.9
NAGS-4	770	195	<1 %	4.95	.003	.012	300	2.8
NAGS-5	510	215	5 %	5.0	.009	.012	290	3.8
NAGS-5	785	207	0 %	5.0	.098	*	275	2.7

* Too high to be measured.

DISCUSSION OF THE DATA (Continued)

a liquid phase to be present. It is not necessary for a liquid phase to exist for the theory to hold but the results would possibly occur faster if one did exist.

For the moment, let us assume that it does. As the grains grow and engulf their neighbors, the liquid phase that exists at the surface will sweep through the neighboring grains. As these grain boundaries move, it is possible that they create a compositional gradient through the grain. We would expect $NiAl_{2-x}Fe_xO_4(x < 1)$, for instance, to have a lower solubility than a more rich spinel. In the case of the NAGS system, the grain boundary spinel most probably would be a lower melting nickel ferrite or nickel gallium ferrite, which may be liquid. If the grain boundary spinel, in the extreme case, is a nickel ferrite, it would have a much higher saturation magnetization than the initial composition. The effect on the saturation would depend upon the amount of grain boundary spinel present and would vary depending upon the firing condition. It would be expected that for a given composition, once the material is fired high enough, some equilibrium condition may be exhibited so that even if the material is fired still higher, no larger amount of grain boundary phase is present. For example, if we examine the data for NAGS-3 and NAGS-4, we find that when the porosity is greater than 5 percent and no appreciable grain growth is expected the saturation magnetization of NAGS-3 is 550 gauss and both the 20 Mc and S-band loss tangent are low (.003). As the porosity is decreased to below 5 percent but not less than one (1) percent the saturation magnetization of NAGS-4 is 605 gauss and the S-band loss is .009. When both

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DISCUSSION OF THE DATA (Continued)

NAGS-3 and NAGS-4 are fired to porosity below one (1) percent and appreciable grain growth is expected the saturation has increased to 770 gauss and the S-band tan δ has increased to above .01. The higher loss tangent probably results from the instability of Fe^{3+} in the liquid phase.

The same results were obtained with NAGS-5 which was stoichiometric; that is, an increase in saturation and loss with a decrease in porosity. The 20 Mc and S-band tan δ were much higher than NAGS-3 which had the same substitution of aluminum and gallium as NAGS-5 but was iron deficient. This increase in tan δ is probably due to the fact that after milling, the composition was no longer stoichiometric but iron excess because of iron pick up during milling. This iron pick up could easily contribute to the tan δ.

Whether this explanation is correct or not, it can be concluded that until further information is available, in order to obtain the saturation magnetization expected for a given composition in this sytem, and in order to keep the S-band tan δ less than .005, it is necessary when processing these materials conventionally to fire them so that grain growth is inhibited and a given amount of porosity (approximately 5 percent) is present in the material. If this explanation is correct, the hot pressing of low loss fine grained powders should permit preparation of samples with less than 5 percent porosity.

In order to study the effects of ceramic processing, it was necessary to select a composition for these experiments. As was mentioned previously, NAGS-4 has been selected as the composition which will be used to determine

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DISCUSSION OF THE DATA (Continued)

what effects ceramic processing has on its properties. NAGS-1 and NAGS-2 were eliminated from further consideration because of the low Curie temperature. NAGS-5 was not considered further due to the high 20 Mc and S-band tan δ. The data obtained again confirmed the desirability of making ferrites slightly iron deficient.

Composition NAGS-3 and NAGS-4 both meet the basic requirements of the saturation magnetization about 600 gauss, Curie temperature approximately 200°C and a loss tangent of less than 0.005. The loss tangent at S-band for NAGS-4 was just slightly higher than the 20 Mc loss. This high loss was attributed to the fact that none of the samples of NAGS-4 that were measured had a porosity of greater than 3 percent. It is felt that with just a slightly higher porosity the S-band loss will come down. In addition, it is possible that sample size played a role. The Curie temperature of NAGS-4 is about 10°C higher than NAGS-3. Since it is anticipated that the tan δ at S-band of NAGS-4 should eventually be at least as low as that of NAGS-3, and the Curie temperature is higher, NAGS-4 was selected as the composition that will be used to study the effect of ceramic processing. If, after more information is obtained, it is found that NAGS-4 is not the proper composition, the processing information gained should be applicable to the similar composition NAGS-3.

Figure 6 is a plot of dielectric constant (ϵ') vs. porosity of all samples of NAGS-1 through NAGS-5. It is easily seen that the porosity

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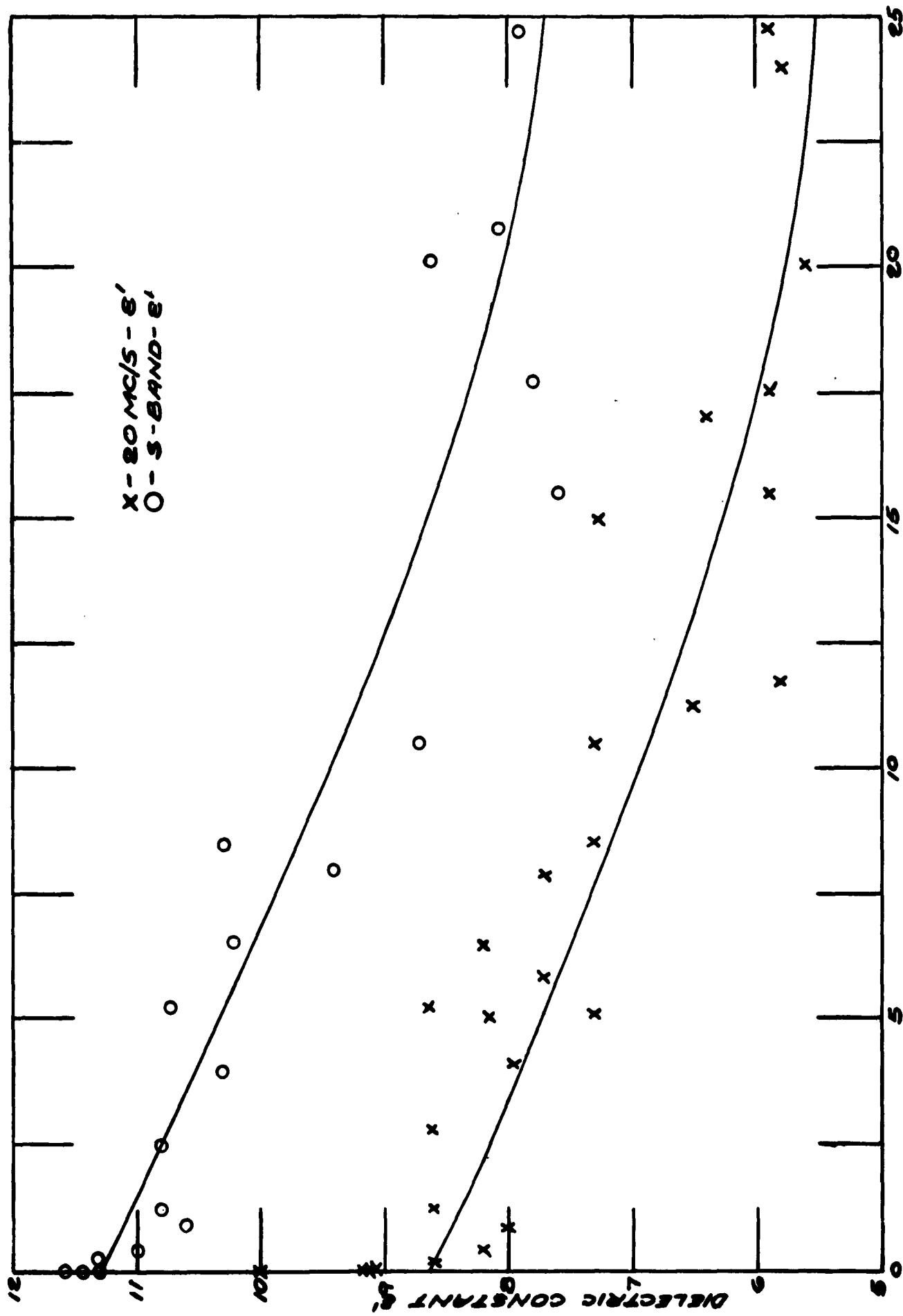
FIG. 6

Dielectric Constant vs. Porosity

DISCUSSION OF THE DATA (Continued)

increases approximately linearly with a decrease in porosity. This is to be expected. The dielectric constant is a bulk measurement and the ϵ' one obtains is an average between the dielectric constant of the material and the dielectric constant of air in the pores. The curve for ϵ' versus porosity at S-band is of the same shape but displaced to higher values of dielectric constant. This may be due in part to the measuring technique used at S-band. It was shown in the measurement, Section 4.1, that the values obtained for this diameter rod of alumina and TT-414 were slightly high, and decreased as the diameter was reduced. The difference in ϵ' between two frequencies may also be due in part to the formula used to calculate ϵ' at 20 Mc. These formulas are based on the ASTM report for measuring high dielectric constant materials. These formulas as shown in Section 3.2.2, page 15, of the First Interim Report contain several correction factors for fringing effects and stray field which may not be valid for these materials and some modification of this formula for ferrites may be necessary. Some of the differences in ϵ' for the two frequencies may be real.

5.2 Flame Spraying

The flame spray experiments described in Section 3.3 were undertaken to work out the flame spray technique required for the nickel aluminum gallium system and to compare the properties of the flame sprayed material to those of conventional prepared ferrites. Of the four batches that have been flame sprayed, only NAGS-5-2, NAGS-5-3, and NAGS-6-1 have been evaluated.

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DISCUSSION OF THE DATA (Continued)

Those compositions have the same alumina and gallium substitution as NAGS-3. Flame sprayed NAGS-5 is stoichiometric and NAGS-6 is slightly iron deficient. The data obtained are given in Table II.

Powder collected from the sidearm from the flame spray run of NAGS-5-2 was pressed into bars at two different pressures (10,000 psig and 20,000 psig). Both bars were fired at 1400°C for 5 hours in oxygen (Firing No. 1039). It is noted that all the properties measured were essentially the same indicating that the pressing pressure did not effect these properties. It should also be noted that the 20 Mc loss tangent was much lower than the conventionally prepared NAGS-5. The loss tangents are 0.003 compared to 0.009. This would tend to confirm the fact that the conventionally prepared material did pick up iron during the milling operation, which contributes to the loss.

The powder from the three sections of collection, sidearm (Sa), scrubber tank (Ta), and the fines carried as overflow from the scrubber tank into bottles (Fi), were prepressed at 250,000 psi, granulated and pressed into bars at 6,000 psi. These bars were then fired at 1350°C for 10 hours in oxygen (firing no. 1050). In any device where powder is carried along in an air stream, we would expect the heavier particles to drop first and the lightest particles to fall last. And so it is in the flame spray apparatus. We expect considerable differences in particle size between the sidearm (Sa) and the tank (Ta) and from the bottles (Fi). This expectation can be confirmed by examining the data for the bars fired at 1350°C (firing no. 1050). These bars were made

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TABLE II

Physical Properties of Flame Sprayed Materials

Sample No.	A.S.G.	%Por.	Bulk Den.	%L.S.	20 Mc K	20 Mc D	S-band K	S-band D	ΔH X-band	T_c Gray.	$4\pi M_s$	"g"
NAGS-5-2-Sa-1039 *	5.04	11.8	4.13	19.5	5.8	.003	--	--	342	184	532	3.30
NAGS-5-2-Sa-1039 **	5.14	11.3	4.18	17.8	6.5	.005	--	--	268	184	537	3.34
NAGS-5-2-Sa-1050	4.94	17.0	4.19	23.7	6.4	.003	--	--	380	186	571	3.25
NAGS-5-2-Ta-1050	4.72	5.1	4.48	27.2	7.3	.028	--	--	384	203	513	3.31
NAGS-5-2-Fi-1050	4.84	5.1	4.58	27.0	8.15	.026	--	--	390	239	619	2.91
NAGS-5-3-Sa-1085	4.96	7.4	4.50	18.0	6.86	.005	9.47	.005	262	183	658	2.96
NAGS-6-1-Fr-1047	4.95	24.8	3.88	19.9	5.97	.009	7.96	.007	336	184	730	2.8
NAGS-6-1-Ba-1047	4.98	20.8	3.99	19.2	6.13	.016	8.01	.007	354	184	722	2.75
NAGS-6-1-Fr-1050	4.92	3.8	4.68	24.0	7.96	.013	10.2	.009	294	182	725	2.8

* Pressed at 10,000 psig.

** Pressed at 20,000 psig.

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DISCUSSION OF THE DATA (Continued)

from material collected from the above mentioned three places. The data for the sidearm material agrees closely with the data of same material fired previously (firing no. 1039). The evaluation of the bar of the tank and bottle material shows some interesting results. The saturation magnetization did not change appreciably but the loss tangent did increase by an order of magnitude and the Curie temperature increased. In fact the data agree very closely with the data for the conventionally prepared material. This would suggest a compositional change, and that the material in the tank and in the bottles is slightly iron excess. We will attempt to confirm this result by chemical analysis in the coming quarter.

A sample of flame sprayed NAGS-5-3-Sa was fired (number 1085) at similar conditions, 1350°C for 10 hours in oxygen. There were some differences obtained in porosity, bulk density and shrinkage as compared to the 1350°C firing of NAGS-5-2. This was due to the higher flame temperature obtained by the use of two burners during the flame spraying of this batch. The magnetic properties measured were very similar to those obtained for the previous flame sprayed batch of this composition. Note the fact that the 20 Mc/s tan δ and the S-band tan δ are the same.

Two firings were made with bars of flame sprayed NAGS-6-1. These firings were at 1350°C and 1265°C for 10 hours in oxygen (number 1050 and 1047 respectively). The bars were made from powder collected from the front (Fr) and back (Ba) of the sidearm. There was little difference in the ceramic pro-

DISCUSSION OF THE DATA (Continued)

perties between the front and the back of the sidearm when fired at the same temperature. There was an expected difference in properties between the two firing conditions. For equivalent materials the dielectric constant and tan δ (both 20 Mc/s and S-band) both increased with increased firing temperatures. It is noted, however, that the S-band and tan δ is lower in all cases than the 20 Mc/s tan δ.

At this time, no explanation can be given for the high loss and high saturation magnetization obtained for composition NAGS-6. Chemical analysis of this material will be made to see if the resultant composition is the same as it was prepared; that is, iron deficient.

In conclusion, it can be seen that the nickel aluminum gallium system can be flame sprayed. The material collected in the sidearm has a low dielectric loss tangent and all the properties of this material are approximately what would be expected for the starting composition. It will be possible to prepare material of this type for use in a phase shift device to ascertain the effect of the fine grained ferrite on the high power characteristics and compare it to a material prepared by conventional ceramic techniques.

5.3 Hot Pressing

During this quarter, several hot pressing runs were made as described in Section 3.4. These runs were made to gain a better insight into the hot pressed sintering of conventionally prepared material and flame sprayed materials. The data obtained for hot pressing runs 23, 24, and 25 are listed in Table III. With

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TABLE III

Sample No. and Composition	A.S.G.	% Por.	Bulk Den.	K (20 Mc)	D	ΔH X-band	"g"	Γ_c Grav.	$4\pi Ms$
HP-23 NAGS-4-2 $Ni_{0.98}Mn_{0.02}Al_{0.728}Ga_{0.247}Fe_{0.924}O_4$ Conventionally Prepared Material	5.09	8.5	----	7.5	.002	528	2.65	255	860
HP-24 NAGS-6-1-Ta $Ni_{1.00}Ga_{0.266}Al_{0.732}Fe_{0.98}O_4$ Flame Sprayed Material	4.90	0.6	4.80	16.7	0.39	297	2.6	210	741
HP-25 NAGS-5-2-Ta $Ni_{1.00}Ga_{0.266}Al_{0.732}Fe_{0.98}O_4$ Flame Sprayed Material	4.86	20.9	3.85	7.0	0.024	400	2.98	223	586

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DISCUSSION OF THE DATA (Continued)

just a few exceptions which will be noted, the ceramic and magnetic properties were in close agreement with the properties obtained by conventional sintering techniques. The 20 Mc/s tan δ values were very close to the values obtained by conventional sintering.

The material used for hot pressing, from the flame sprayed batches, was from the tank. If as suspected, there is a composition deviation from the starting formulas in the direction of excess iron, the high loss for HP-24 and HP-25 can be attributed to this excess iron. This would also account for the high Curie temperature. The fact that the hot pressing is accomplished at much lower temperatures (1150°C - air) than conventional sintering (1350°C - oxygen) may not allow some of the excess iron to be oxidized. This would explain the higher loss in the hot pressed sample as compared to the conventionally sintered sample. The chemical analysis of these materials should help to clarify this situation.

The values obtained for linewidth and g were in good agreement with the sintered bars. The saturation magnetization obtained also was in good agreement with the conventionally sintered material except for the value obtained for HP-23 (NAGS-4). No explanation is apparent for this increase at this time. The major disagreement between the hot pressed samples and the sintered bars is the Curie temperature. The Curie point is consistently high in all hot pressing experiments. At the present time, the only explanation that can be given is that there is a compositional variation in the material, probably

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DISCUSSION OF THE DATA (Continued)

incomplete reaction. Even though no definite conclusion can be drawn as to why the Curie temperature is high, as long as the materials work in a device this consistent increase in Curie temperature can only help the operation of the device.

5.4 Annealing Experiments

Based on some preliminary annealing experiments reported previously, several samples were annealed at 1050°C for 144 hours in an oxygen atmosphere. The data obtained are listed in Table IV.

The behavior of the saturation magnetization before and after annealing is very erratic. Some samples increase while others decrease. All compositions were originally formulated to yield the same saturation, but this was not obtained. It is seen, however, that the annealing of these samples did bring the saturation magnetizations between samples closer together. Where before annealing, the saturation ranged from 510 to 785 gauss, after annealing the range was from 570 to 793 gauss.

In general, the Curie temperature and the tan δ either remained unchanged or decreased with annealing. The only exception was the increase in tan δ for the flame sprayed NAGS-6 after annealing.

It is evident that the results obtained after annealing are very erratic and inconclusive. Since these experiments are very time consuming and require considerable re-evaluation of the materials, and since no trend can be established, it is felt that further work at this time would be less than fruitful. It is possible that the erratic results often are due to slight changes in site

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TABLE IV

NAGS Sample	Properties Before Annealing			Properties After Annealing		
	$4\pi M_s$	T_c	20 Mc/s Tan δ	$4\pi M_s$	T_c	20 Mc/s Tan δ
2-2-952	730	158	.003	745	158	.002
2-2-975	576	167	.001	599	157	.0008
3-3-952	770	182	.003	787	181	.003
3-3-975	760	189	.002	663	178	.0002
4-2-952	770	190	.002	793	188	.002
4-2-975	605	197	.002	646	192	.0006
5-1-952	785	201	.098	719	203	.104
5-1-975	510	211	.009	656	203	.009
5-2-Sa-1050	571	186	.003	570	180	.003
5-2-Ta-1050	513	203	.028	627	200	.037
5-2-Fi-1050	619	239	.026	738	214	.024
6-1-Fr-1050	725	182	.013	742	175	.04
6-1-Fr-1047	730	184	.010	752	176	.03
6-1-Ba-1047	722	184	----	760	179	.03
HP-19	765	315	.012	737	241	.001
HP-20	740	320	.018	729	238	.004

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DISCUSSION OF THE DATA (Continued)

preference of Ga and Al in the material. Therefore, depending on the inhomo-geneity of the composition present, annealing could make the saturation go either up or down.

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6. SUMMARY

The initial requirements of a saturation magnetization of 600 g, Curie temperature of 200°C and a tan δ of less than 0.005 have been approximately met by two compositions, NAGS-3 and NAGS-4. Since NAGS-4 has a higher Curie temperature (195°C), NAGS-4 has been selected for further study.

A series of experiments have been started to study the effect of ceramic processing on the ceramic and magnetic properties so that a better insight can be obtained as to the behavior of these materials.

The problem mentioned in the last report in which the cavity Q was increasing instead of decreasing when low loss samples were measured has been resolved. The improper behavior was due to the fact that the coupling holes in the cavity were not small enough so that the required condition of external Q_e was not met. The diameter of the coupling holes was decreased so that the required condition of Q_e is now met.

Samples of known low loss materials were evaluated at S-band. These materials had saturation magnetization of approximately 1400 g and 2000 g. When evaluated at S-band the tan δ's were unusually high. Measurements of tan δ have been started as a function of diameter. It indicates that when a sample has a high saturation and the diameter is large the rod is not in a part of the cavity where the H field is zero. These experiments are continuing and may give some insight into the high S-band loss tangent for the high saturation magnetization materials, i.e., greater n 700 gauss.

A theory has been proposed as to why the saturation magnetization of these materials drastically increases when the porosity of the sample is less than

SUMMARY (Continued)

five (5) percent. This phenomenon has been attributed to the grain growth mechanism involved and the formation of a composition gradient across a grain when the grain growth energy is reduced due to the removal of much of the internal porosity.

Several batches have been flame sprayed and the properties of the material collected in the sidearm agree quite closely with the properties obtained on conventionally prepared material. The fines collected in the tank and from the scrubber of the flame sprayer had high 20 Mc loss tangent. This may be due to compositional variation in the material. Chemical analysis of this material will be performed to determine if composition variations (primarily excess iron)are the possible cause of the high tan δ's.

Several hot pressing runs were made and the data obtained indicate that properties of these materials are in agreement with the properties obtained on identical material conventionally sintered. The only major disagreement is that the material that is hot pressed has consistently yield higher Curie points than conventionally sintered materials. No conclusive explanations can be given for the anomaly at this time.

The annealing experiments have shown to be very erratic and have not indicated any trend or conclusive results. Because of this and since they are very time consuming, it has been decided to discontinue the annealing experiments at this time.

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7. PROGRAM FOR NEXT INTERVAL

During the next quarter, the following work will be performed:

1. Complete the processing study on NAGS-4 and evaluate these materials.

2. Hot press NAGS-4 to obtain the optimum hot pressing condition which will be used to hot press large bars of NAGS-4.

3. Prepare a large batch of NAGS-4 to be used for the hot pressing experiments of large bars.

4. Complete the large hot pressing die and hot press samples of NAGS-4.

5. Continue flame spray experiments on NAGS-3, and NAGS-4 and evaluate these materials.

6. Complete the study of the effect of sample diameter on the loss tangent at S-band for high saturation magnetization materials. Change the diameters on some NAGS's with saturation over 600 gauss to observe if the tan δ at S-band is affected.

7. Complete the line shape apparatus and measure low field loss of NAGS samples.

8. Complete the high power apparatus and measure onset of non-linearity in small samples by observing the deterioration of the trailing edge of the transmitter pulse.

9. Measure phase shift of the NAGS samples in the ridge guide phase shifter.

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8. IDENTIFICATION OF PERSONNEL

Below is a list of the personnel working on this contract and the hours spent. The time has been recorded as to the amount supported by Airtron and the Government.

HOURS SPENT ON FERRITE DEVELOPMENT CONTRACT

October 18, 1962 to January 18, 1963

Name	Airtron	Government
J. W. Nielsen	27	105.0
M. King	12	
D. Blake	240	
B. Kaplan	246	
S. Cook	6	
G. Townsend		30.3
D. Lepore		449.5
A. Bates		140.0
A. Wheeler		47.5
A. Dort		57.0
B. Connolly		54.5
J. Zneimer		200.0
TOTAL HOURS	531	1083.8

9. **PROJECT PERFORMANCE AND SCHEDULE CHART**

Figure 7 is the Project Performance and Schedule Chart.

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AIRTRON, A DIVISION OF LITTON INDUSTRIES

PROJECT PERFORMANCE AND SCHEDULE

Contract No. Nobsr 87388　　　(Report)　DATE:　February 4, 1963

Figure 7　Project Performance and Schedule Chart

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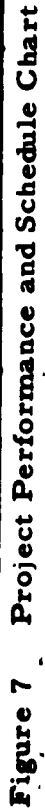
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